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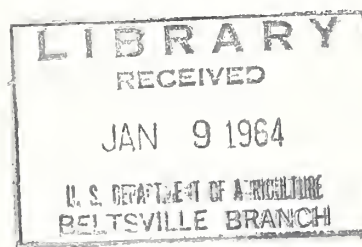
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# ON DIFFUSION LAWS APPLIED TO POROUS MATERIALS <sup>1/</sup>

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In 1855 Fick (4)<sup>3/</sup> put diffusion on a theoretical basis by showing that the diffusion of substances through solutions obeyed the same mathematical laws that Fourier had derived for the conduction of heat in solids. Since the time of Fick, theoretical and experimental aspects of diffusion have undergone spectacular advances both in single- and multiphase systems (1, 9). For a multiphase system such as a porous material, diffusion takes place almost exclusively through the fluid phase (gas or liquid or both). The solid matrix complicates matters by altering the diffusion path length and the cross-sectional area available for diffusion.

The diffusion path length and the effective cross section are extremely complicated properties of each porous material, and, in certain cases, both may be functions of space and time. Accounting for these factors in diffusion equations is usually accomplished by inclusion of the two parameters, porosity and tortuosity, which are assumed to be constants. The manner in which the two parameters have been used in diffusion equations has not been universal. Furthermore, the adequacy of the two parameter treatment has been questioned (2, 6, 10).

It is the purpose of this report to bring together the several approaches that have been used to account for the complications caused by the porous material and to show the relationships, and some limitations, of the several concepts.

The discussion is confined to diffusion equations applied to porous materials. Adequate reviews of diffusion processes are available (1, 8, 9). We assume isothermal conditions and that the volume of the porous medium remains constant.

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<sup>3/</sup> Underscored numbers in parentheses refer to Literature Cited, p. 10.

## FIRST ORDER EQUATIONS

Quantitative measurements of the rate at which a diffusion process occurs are usually expressed in terms of a diffusion coefficient. For brevity, we will confine our discussion to one dimension, and define the diffusion coefficient as the rate of transfer of the diffusing substance across a unit cross-sectional area divided by the space gradient of concentration of the substance at the section. Thus, if  $q = Q/t$  is the amount of substance transferred in time  $t$ ,  $A$  the cross-sectional area,  $c$  the concentration, and  $x$  the space coordinate, then

$$q = - DA \frac{\partial c}{\partial x} \quad [1]$$

is a definition of the diffusion coefficient  $D$ . This definition can be unambiguous only if the units of  $q$ ,  $A$ ,  $c$ , and  $x$  are carefully specified (8). As Hartley and Crank (8) have noted, concentrations can be expressed in a number of different ways, thus necessitating that all components of [1] carry an index to indicate the frame of reference used. In general, the concentration  $c$  should have the same quantity reference as  $q$ , and the volume should be of the same length reference as  $A$  and  $x$ . The use of different frames of reference for components of the same equation requires the use of appropriate conversion factors. This is particularly true in porous materials where the frame of reference may be the entire bulk medium (designated by the subscript  $m$ ) or the fluid phase (designated by the subscript  $f$ ). In some cases the fluid phase must be further designated as gas or liquid or both.

Writing equation [1] in reference to the entire porous medium, we have

$$q = - D_m A_m \frac{\partial c_m}{\partial x_m}, \quad [2]$$

where  $q$  refers to the quantity (frequently the mass) of diffusing substance per unit time and does not need to be referred to the medium or fluid reference. If two or more substances are diffusing simultaneously, then the equation can be written for each substance and  $q$  would carry an appropriate index (8).

The use of  $c_m$ , the quantity of diffusing substance per unit volume of porous medium, departs from the more commonly used definition of concentrations, but it is the only correct definition that can be used for a two-component system when one component is the porous medium. Its use is not without precedent (5, 13).

In many systems it is more convenient to measure the concentration with reference to the fluid phase. If  $\epsilon$  is the relative volume ( $V_f/V_m$ )

occupied by the particular fluid in question, then

$$c_m = \epsilon c_f \quad (0 < \epsilon < 1). \quad [3]$$

In the case where a single fluid completely occupies the pores of the medium,  $\epsilon$  is the porosity.

The correct value of  $\epsilon$  may not be evident in every experiment. For example, if dead-end pores are present in the medium (6, 7) and a steady state exists, not all pores contribute to the diffusion path. Hence, the total volume of fluid ( $V_f$ ) may not be the correct parameter to use in calculating  $\epsilon$ . The magnitude of the error involved here is not known. The pertinent literature has appeared only recently, and the data are largely for sandstone models. For our purpose it will suffice to mention the possible complications and assume that  $\epsilon$  is uniquely given by  $V_f/V_m$  and is a constant.

Using [3] in [2] we have

$$q = - D_p A_m \frac{\partial c_f}{\partial x_m} \quad [4]$$

where  $D_p = D_m \epsilon$ .

For gaseous diffusion in porous materials, Penman (11) defined the diffusion coefficient as given by equation [4]. This convention has been widely, but not exclusively (14), used in soils literature.

The usual definition of tortuosity is the ratio of the medium (or externally measured) length to the diffusion path length, i. e.

$$x_m = \beta x_f \quad (0 < \beta < 1). \quad [5]$$

The relationship between  $A_m$  and  $A_f$  has been reported in several different forms:

(a) For diffusion paths of constant cross section that pass directly along a line perpendicular to the surface  $A_m$ ,  $A_f = \epsilon A_m$ . Several investigators have used this form (3, 11).

(b) For diffusion paths of constant cross section that follow a tortuous path through the medium, the following argument can be used. Since  $\epsilon = V_f/V_m = A_f x_f / A_m x_m$ , and using [5], we find  $A_m = A_f (\beta \epsilon)^{-1}$ , a result obtained by several investigators (2, 12, 15).

(c) Diffusion paths that have a nonuniform cross section and also follow a tortuous path through the medium have been discussed by Currie (2). He argued that the effective area available for diffusion may be reduced by constrictions along the diffusion path and treated the



simplest form of this case by assuming that the area along the diffusion paths varies sinusoidally.

The arguments used individually in the above three cases can be combined by reverting to the definition of the diffusion coefficient given by equation [1]. Equation [1] was written for an infinitely thin cross section of area  $A$ . Applying the equation to a porous material, we have an infinitely thin section of area  $A_m$  in which the area available for diffusion is  $\epsilon A_m$ . Consider an infinite number of sections so arranged as to form a volume  $A_m x_m$ . We require each and all sections to have the same porosity ( $\epsilon$ ).<sup>4/</sup> We do not require the "holes" in each section to be of uniform size within a section or among sections, nor for all "holes" to have the same space coordinates among sections. We require that the "holes" interconnect to form a continuous, though tortuous, path of varying cross section through the thickness  $x_m$ . In addition, we have assumed that no dead-end pore volume exists in the medium.

Consider now a pore shaped so that its area increases in the  $x$  direction. Since each infinitely thin section must have a porosity  $\epsilon$ , another pore must exist whose area decreases in the  $x$  direction. The net area of the innumerable pores in the thickness  $\Delta x$  would be constant.

When the area of an individual pore is not constant, the diffusion path length becomes nebulous. Within an individual pore, it is necessary to take some average value for the path length. Thus, instead of a tortuosity factor and another factor accounting for the nonuniformity of area in individual pores, we will consolidate these factors into one "complexity" factor for a porous material and designate this with the symbol  $\alpha$ . The term  $\alpha$  includes  $\beta$  and the factor accounting for nonuniform cross section in an unspecified manner and is associated with length in the same manner as  $\beta$ . We must associate  $\alpha$  with length because, as  $\Delta x \rightarrow 0$  the effective area approaches  $\epsilon A_m$ , and the diffusion paths do not have sufficient length to exhibit a tortuosity nor a nonconstant cross section. For the purpose of this discussion, we will assume that  $\alpha$  is a constant. Then

$$x_m = \alpha x_f, \quad (0 < \alpha < 1) \quad [6]$$

and

$$A_m = A_f (\alpha \epsilon)^{-1}, \quad [7]$$

by the same argument used previously in case (b).

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<sup>4/</sup> It is necessary to make this restriction in order that the area term in the diffusion equations can be considered constant. If it is not constant the functional relationship between  $\epsilon A_m$  and  $x_m$  must be specified before solutions of the equations can be obtained.



Defining  $D_f$  as the diffusion coefficient for a diffusing substance in bulk fluid (departing from the more conventional notation  $D_0$ ) and using [6] and [7] in [4], we find the relations between the diffusion coefficients to be

$$D_p = D_f \epsilon \alpha^2, \quad [8a]$$

and

$$D_m = D_f \alpha^2, \quad [8b]$$

In applying equation [1] to the steady state diffusion of a substance in a porous material of length  $L$ , we need only to require that the flux  $q$  be constant and have the same value at all cross sections within the system. If we require here, as we did in the discussion of the "complexity" factor above, that the area available for diffusion be of uniform value for all sections, then the diffusion coefficient can be evaluated from

$$q/A_m = - D_p \frac{\partial c_f}{\partial x_m}, \quad [9]$$

if the concentration is known as a function of distance. If  $D_p$  is constant, then [9] reduces to the familiar form

$$q/A_m = D_p (c_{f1} - c_{f2})/L \quad [10]$$

where  $c_{f1}$  and  $c_{f2}$  are the concentrations (with reference to the fluid) at the ends  $x = 0$  and  $x = L$ , respectively. Obviously  $c_m$  and  $D_m$  could be used in [9] and [10]. The experimental conditions usually dictate the frame of reference to be used.

## SECOND ORDER EQUATIONS

Consider two sections a distance  $\Delta x$  apart. The flux entering one section is  $q$  and that entering the other is  $q - (\partial q / \partial x) \Delta x$ . Since the rate of accumulation of substance in the layer  $A \Delta x$  is  $A(\partial c / \partial t) \Delta x$ , we have

$$A \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (DA \frac{\partial c}{\partial x}). \quad [11]$$

If the cross section  $A$  is constant, [11] becomes the familiar second order concentration-dependent diffusion equation, viz

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \quad [12]$$

If D is also constant, [12] takes the simpler form

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [13]$$

Equation [13] is known as Fick's second law. The first order diffusion equation, usually written in the form of [1] except with D a constant, is known as Fick's first law. This terminology is probably based on the fact that equation [13] is a second order equation and equation [1] is a first order equation. Fick's original equation had the form of [11] with D constant and the cross section as a function of distance (4). In his first experiment, he utilized equation [13]. For his subsequent steady state experiments, he set  $\partial c / \partial t = 0$  and integrated the right-hand side to obtain  $c = ax + b$ . This is of the same form as [10].

If, in the application of the second order equations to porous materials, the cross section available for diffusion varies with distance, then equation [11] is applicable. The use of [11] would require us to know exactly the functional relationship between A and x. For the majority of applications, it is again convenient to assume a constant effective cross section throughout the material.

For the following discussion, either equation [12] or [13] would serve equally well. We will use [13] for convenience.

Equation [13], written in reference to the entire porous medium, is

$$\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x_m^2} \quad [14]$$

With concentrations expressed on basis of the fluid,

$$\frac{\partial c_f}{\partial t} = D_m \frac{\partial^2 c_f}{\partial x_m^2} \quad [15]$$

Thus, regardless of the concentration reference, the diffusion coefficient is  $D_m$ . If it is more convenient to use  $D_p$  instead of  $D_m$ , then

$$\frac{\partial c_f}{\partial t} = \frac{D_p}{\epsilon} \frac{\partial^2 c_f}{\partial x_m^2} \quad [16]$$

Upon integrating equations [14], [15], or [16],  $c$  should be expressed in both integral and boundary values on the same consistent basis. If the integration yields  $q/A$ , the same length reference, or appropriate conversion factors for  $c$  and  $A$ , should be used.

Comparison of equations [2], [4], [15], and [16] shows that, without properly indexing or otherwise identifying the diffusion coefficients, confusion can arise when data from different sources are compared, since one may report  $D$  and another  $D_m$  without clearly pointing out which was used. An additional complication arises if dead-end pores are present in sufficient numbers to cause the values  $D_m$  (or  $D_p$ ) measured at steady state to be different from values of the same coefficient measured in the transient state (6, 7).

By use of equation [7] in [15] and [16] the same relationship is obtained between the diffusion coefficients as is given in equations [8a] and [8b]. These relationships are valid only when  $\alpha$  and  $\epsilon$  are constants. It has been clearly shown by Currie (2) that  $\alpha^2$  (i.e.  $D_m/D_f$ , his figure 2) and  $\epsilon$  are not simply related. The relationship is influenced, among other things, by particle and pore shapes.

Estimations of the complexity of porous material have been the subject of numerous investigations. The diffusion coefficient (either  $D_m$  or  $D_p$ ) is measured and related to  $D_f$  by equations of the form [8]. For the ratio  $D_m$  (or  $D_p$ )/ $D_f$  to yield a significant value,  $D_f$  must be known with an error less than or equal to that of  $D_m$  (or  $D_p$ ). Values of  $D_f$  taken from the literature may not always be an appropriate basis for comparison. For example, consider the diffusion of an ionic substance through a liquid solution held by a porous material such as soil, and the diffusion in dilute, unconfined, single-salt solutions. It is obvious that a diffusing material encounters radically different chemical and physical environments in the two conditions. Thus, chemical factors, in addition to the physical factors enumerated previously, can enter equations [8a] and [8b] (12). The "complexity" factor is then even more complex than that indicated in the earlier discussion.

It is doubtful that, for diffusion of many substances in soils, the various chemical and physical factors can be separated, evaluated, or enumerated. The data reported in the form of  $D_m$  or  $D_p$  would seem preferable since fewer assumptions must be made, and the physical significance of  $D_m$  and  $D_p$  is less ambiguous than a list of unseparable chemical and physical factors.

The terms  $D_m$  and  $D_p$  are equally meaningful, and the choice of one over the other is dictated by personal preference and experimental conditions. Whatever frame of reference is used to denote the various parameters in the diffusion equations, it should be described unambiguously.

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